

SCIENCE FOR GLASS PRODUCTION

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PROGRAMMING AND CALCULATION OF PROCESS PARAMETERS IN PRODUCTION OF SILICATE MATERIALS

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Fundamental approaches to a mathematical description of the liquidus surface in silicate systems are proposed, which can be used in developing software for operational control of the process parameters in silicate production.

Glass and glass ceramic materials based on basalt and similar rocks find increasingly wide application. In particular, basalt fiber is distinguished by high strength, high chemical resistance, and other valuable properties, which makes this fiber indispensable in several sectors of industry. It would be convenient to use industrial mining waste for this purpose; however, such waste is characterized by a high heterogeneity of its composition and properties. We have demonstrated that the following levels of natural heterogeneity in this waste can be distinguished depending on the type of effect on the technological processes:

- the crystalline-chemical level determined by differences in the chemical composition and properties within a crystalline individual; such heterogeneity can influence the concentration process but has no effect on the production technology of construction materials;
- the mineralogical level related to different properties within the same rock; the negative effect of such inhomogeneity can be eliminated by preliminary preparation of materials (homogenization);
- the petrographic level determined by variations in the properties of a mineral in different parts of the bed; to decrease the negative effect of such heterogeneity, special technical measures such as averaging are required;
- the geological level determined by the presence of different grades and types of a mineral within the same deposit or ore field; elimination of the negative effect of such heterogeneity calls for the development of special technologies.

The industrial mining wastes studied by us had heterogeneities at all levels, and whereas the effect of heterogeneities at the geological and petrographic levels can be eliminated in the course of primary preparation of materials and controlling the material quality, the negative effect of inhomogeneity at the mineralogical and especially at the crystalline-chemical levels cannot be fully eliminated. In this context, operational control of the technological process is required.

The temperature of complete batch melting is of special significance in the production of glass and glass ceramics. If unmelted crystalline phases are contained in incompletely melted glass, local stresses arise in the finished product. The presence of even a small quantity of crystalline phases may significantly deteriorate the external appearance of finished articles and decrease their mechanical strength.

In using traditional materials, the batch composition and the process temperature are selected in such a way as to avoid the emergence of the crystalline phase in the course of glass melting. However, this condition cannot always be satisfied in producing glass or glass ceramics from mining waste due to the unstable composition of the material recycled. For the operational control of the process, it is necessary to assess the degree of the effect of variations in the mineral and chemical compositions of the material on the temperature of complete melting.

Most binary and many ternary systems within the limits of the basaltoid melt field ($\text{CaO} - \text{MgO} - \text{Al}_2\text{O}_3 - \text{Fe}_2\text{O}_3 - \text{Na}_2\text{O} (\text{K}_2\text{O}) - \text{SiO}_2$ system) are well studied and represented as phase diagrams [1, 2]. However, this form of representing the liquidus temperature is not very convenient for current practical control of the batch preparation process and the

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melting and working temperature. With respect to binary and ternary systems, this form allows for fast determination of the liquidus temperature for any glass composition, but with significant errors. However, in the case of a four-component system, such determinations are neither accurate nor fast.

Methods for mathematical description of property-versus-composition dependences for multicomponent systems have been developed in recent years [3–6]. This problem can be relatively easily solved for simple binary eutectic systems. In particular, I. B. Bobylev and V. N. Anfilogov [7–9] proposed a method for the calculation of the liquidus line for oxide – orthosilicate binary systems using the Schroeder – Van Laar equation:

$$\ln N = \left[-\Delta H_m \left(\frac{1}{T} - \frac{1}{T_m} \right) \right] R,$$

where N is the molar part of the component crystallizing in the particular segment of the phase diagram; ΔH_m and T_m are, respectively, the enthalpy and melting temperature of the particular component.

According to the data of these authors, silicate melts, in accordance with a polyelectrolyte model, are semi-ideal mixtures, and the above equation can be applied to them without replacing the concentration with the activity. However, such calculation involves certain difficulties even for the simplest cases. This is related to the fact that melting of orthosilicate is accompanied by its partial decomposition into a metal oxide and more complex polymer forms. Furthermore, data on melting enthalpy are missing for many compounds, even for binary systems. Therefore, the authors observe that the main advantage of the proposed calculation scheme is not knowledge of the liquidus temperature but the possibility to determine the concentrations of simplest polymeric forms in silicate melts.

Vast opportunities are provided by a mathematical description of the liquidus line or the liquidus surface for binary, ternary, and multicomponent systems based on experimental data [3]. Such calculations for simple eutectic systems do not present significant difficulties. Ternary systems, for instance, $X-Y-Z$ systems, with a small exception are approximated by equations of the following form:

$$T_z = Ax^2 + By^2 + Cxy + Dx + Ey$$

or

$$T_z = Ax^2 + By^2 + Cxy + Fx^2y + Gxy^2 + Dx + Ey,$$

where T_z is the estimated temperature within the bounds of the crystallization field of the phase z ; x and y are the weight contents of the phases x and y , %.

For instance, the system $\text{CaO} - \text{MgO} - \text{Al}_2\text{O}_3 - \text{Fe}_2\text{O}_3 - \text{FeO} - \text{Na}_2\text{O} (\text{K}_2\text{O}) - \text{SiO}_2$ is characterized by a large quantity of intermediate two-, three-, and four-component mineral phases and binary and triple eutectics; consequently, the

problem of a mathematical description of the liquidus surface within the limits of this system is difficult to solve. At the same time, a basaltoid composition has a relatively narrow variation interval of the SiO_2 content; therefore, in most cases basaltoids do not go beyond the bounds of the pyroxene – feldspar (quartz) – (magnetite) field or the albite $\text{NaAlSi}_3\text{O}_8$ – anorthite $\text{CaAl}_2\text{Si}_2\text{O}_8$ – sodium silicate $\text{Na}_2\text{Si}_2\text{O}_5$ – wollastonite CaSiO_3 – ferrosilite FeSiO_3 – enstatite MgSiO_3 – silica minerals (quartz, tridimite, cristobalite) SiO_2 field. Therefore, we restricted ourselves to describing the liquidus surface within a sequence of the most abundant ternary (and pseudoternary) systems that do not go beyond the bounds of the specified field.

The successive approximation method was used for the mathematical description of the system. The description of the liquidus surface in a ternary system $A-B-C$ started with a description of the liquidus lines of the binary systems $A-B$, $A-C$, and $B-C$. The liquidus line for the $A-B$ binary system on the segment from A to the double eutectic was described by the equation

$$t = t_a + k_{b1}B + k_{b2}B^2 + \dots + k_{bn}B^n, \quad (1)$$

where t is the estimated liquidus temperature, °C; t_a is the melting point of the mineral phase A , °C; B is the weight content of the phase B , %; k_{b1} , k_{b2} , ..., k_{bn} are the dimensionless coefficients.

The liquidus line on the segment from B to the eutectic was described by the equation

$$t = t_b + k_{a1}A + k_{a2}A^2 + \dots + k_{an}A^n,$$

where t_b is the melting temperature of the mineral phase B , °C; A is the weight content of the phase A , %.

In the case of a simple eutectic system, a higher temperature value is true for any point of the composition. It was first assumed that each branch of the liquidus line can be described by a first-order equation. The regression equation coefficients were calculated using the least squares method. If the maximum deviation of the estimated temperature values from the experimental values did not exceed 10°C, it was considered that the equation adequately describes the liquidus line.

With larger deviations, the liquids line was described by a second-order equation. Then the procedure was repeated. If the discrepancies between the experimental and the estimated data again exceeded 10°C, the liquidus line was described by a third-order equation, etc. In most cases the second-order equations yielded satisfactory convergence.

In rare cases where the deviation of the estimated data from the experimental values in the description of the liquidus line was not of a specific pattern, trigonometry functions were used. If the crystallization field of a third phase was observed within the limits of a binary system, the liquidus surface within this field was described by an additional equation.

After the description of the liquidus lines in the binary systems is completed, it is possible to pass to describing the liquidus surface in ternary systems. The equation describing the liquidus surface for the $A-B-C$ system within the limits of the crystallization field of the component A will have the following form:

$$t = t_a + k_{b1}B + k_{b2}B^2 + \dots + k_{bn}B^n + k_{c1}C + k_{c2}C^2 + \dots + k_{cn}C^n + k_{bc1}BC + k_{bc2}B^2C + k_{bc3}BC^2 + \dots + k_{bcm}B^nC^n. \quad (2)$$

Comparing Eqs. (1) and (2), one can conclude that

$$\Delta t = k_{bc1}BC + k_{bc2}B^2C + k_{bc3}BC^2 + \dots + k_{bcm}B^nC^n,$$

where Δt is the difference between the liquidus temperature (or the experimental temperature) in a particular point not lying on the side of the triangle ABC and the estimated value of this parameter calculated from the binary system equations.

Having calculated the latter value for each composition, for which the experimental temperature of complete melting is known and having calculated Δt , it is possible to determine the coefficients $k_{bc1}, k_{bc2}, k_{bc3}, \dots, k_{bcm}$. Similarly to the previous cases, this calculation was made by the successive approximation method. It was first assumed that the surface can be described by a second-order equation and $\Delta t = k_{bc1}BC$. If the deviations of the estimated temperature values from the experimental ones did not exceed 10°C , the calculations ended. With larger deviations, the assumptions of an equation of the third, fourth, etc. order were investigated.

In processing the available experimental data on the liquidus temperatures and the viscosity logarithms under a preset temperature, their relationship with the composition was approximated by polynomials of the n th degree.

To assess the true value of the parameters taking into account the required reliability level, it is possible to determine the confidence interval depending on the quantity of available experimental points and the degree of the polynomial:

$$b_j \pm t_j \sqrt{\frac{S}{(n-j-1)H_j}},$$

where $t_j = t(P, k)$ is the Student criterion for the number of degrees of freedom $k = n - j - 1$ [10]; S is the sum of the squares of the deviations of the experimental points y_i from the estimated points $p_j(x_i)$; $S = \sum_{i=1}^n [y_i - b_0 p_0(x_i) - b_1 p_1(x_i) - \dots - b_v p_v(x_i)]$; $H_j = \sum_{i=1}^n p_j^2(x_i)$.

In this case all measurements are assumed to be equally precise and independent with normally distributed errors.

Thus, the confidence interval is determined by the number of degrees of freedom, which, in turn, depends on the number of experimental points and the degree of the polynomial.

The lower boundary of the confidence probability is equal to 0.9 (or 90%), and the minimum number of degrees of freedom is equal to 4. Assuming a degree of the polynomial equal to 1 (i.e., a linear dependence), the minimum number of experimental points is equal to 6. As the degree of the polynomial increases, the number of degrees of freedom decreases, which increases the confidence interval.

Thus, with confidence probability 0.9 and the number of the degrees of freedom equal to 4, the confidence interval will be

$$b_i \pm 1.066 \sqrt{\frac{S}{H_j}},$$

and with the number of degrees of freedom equal to 9

$$b_i \pm 0.611 \sqrt{\frac{S}{H_j}},$$

i.e., the interval increases $2 \times 1.74 = 3.48$ times with the number of degrees of freedom decreasing by 5 ($9 - 4$).

With the confidence probability 0.95 these coefficients, respectively, are equal to 1.388 (with the number of the degrees of freedom equal to 4) and 0.754 (the number of degrees of freedom equal to 9), i.e., a decrease in the number of the degrees of freedom by 5 results in $2 \times 1.84 = 3.68$ times growth of the confidence interval.

With a sufficiently large number of the experimental points, the degree of the polynomial can be increased to achieve a higher accuracy, and in the case of an insufficient quantity of the experimental data, it makes sense to restrict oneself to a linear dependence, since a decreased number of degrees of freedom will increase the confidence interval, i.e., will decrease the precision and increase the approximation error.

Fluctuations in the chemical and mineral composition of the material can influence other important process parameters as well, in particular, the melt viscosity. The viscosity of melts and glasses has an effect on such important process parameters as the temperatures of melting, clarification, working, and annealing of glass. Furthermore, fluctuations in the composition lead to fluctuations of various significant properties of the finished products, in particular, their TCLE and acid and alkali resistance. A variation in the composition can affect the liquation process and thus influence the decorative properties of the material.

The authors have summarized data on the effect of variations in the initial material composition on the properties of the batch, melt, and finished glass and glass ceramic materials in the quartz – albite (orthoclase, microcline) – anorthite – diopside – enstatite – magnetite systems corresponding to natural basalt, diabase, gabbro, norite, pyroxenite, and other basic and hyperbasic rocks. These data can serve as the basis for the mathematical description of property-versus-composition dependences required for the automation of the calcu-

lations of such systems and the development of software programs for fast control of the process parameters in production of glass and other silicate materials with prescribed properties.

The Institute of Chemistry has developed a program for calculating the process parameters in the mineral fiber production, has tested this program at the Severonikel Integrated Works, and has obtained positive results.

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